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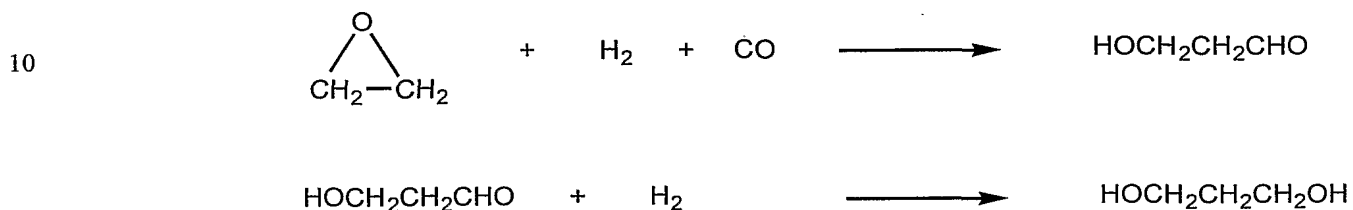
(54) Title: PROCESS FOR THE PREPARATION OF PROPANE-1,3-DIOL BY VAPOR PHASE HYDROGENATION OF 3-HYDROXYPROPANAL, BETA-PROPIOLACTONE, OLIGOMERS OF BETA-PROPIOLACTONE, ESTERS OF 3-HYDROXYPROPANOIC ACID OR MIXTURES THEREOF

(57) Abstract: A process is described for the production of propane-1,3-diol. The process comprises subjecting a vaporous feed mixture comprising a hydrogen-containing gas and a feedstock selected from 3-hydroxypropanal, β -propiolactone, oligomers of β -propiolactone, esters of 3-hydroxypropionic acid, and mixtures of two or more thereof to hydrogenation conditions in a hydrogenation zone in the presence of a heterogeneous hydrogenation catalyst, and recovering a reaction product comprising propane-1,3-diol.

PROCESS FOR THE PREPARATION OF PROPANE-1,3-DIOL BY VAPOR PHASE HYDROGENATION OF 3-HYDROXYPROPANAL, BETA -PROPIOLACTONE, OLIGOMERS OF BETA -PROPIOLACTONE, ESTERS OF 3-HYDROXYPROPANOIC ACID OR MIXTURES THEREOF

This invention relates to the production of propane-1,3-diol.

Propane-1,3-diol is used as an intermediate in the production of polyesters for production of fibres or films. It can be prepared by a two-step process in which ethylene oxide is subjected to an oxonation reaction followed by hydrogenation:



United States Patent Specification No. 5,981,808 describes the use of a non-phosphine-ligated cobalt compound as oxonation catalyst in an essentially non-water-miscible solvent followed by water extraction to separate the catalyst from the 3-hydroxypropanal produced as oxonation product. The aqueous mixture containing the 3-hydroxypropanal is then subjected to hydrogenation. United States Patent Specification No. 5,585,528 proposes addition of a lipophilic tertiary amine as a promoter in such a process. Use of methyl t-butyl ether for extraction of the aqueous mixture to recover cobalt catalyst for re-use is described in United States Patent Specification No. 5,770,776. United States Patent Specification No. 5,786,524 teaches a similar process and proposes the use of a rhodium catalyst as an alternative catalyst in the oxonation step.

It is, however, a drawback of such a process that high levels of byproducts are produced during liquid phase hydrogenation of the intermediate 3-hydroxypropanal under the recommended hydrogenation conditions, namely liquid phase hydrogenation at 220°C and 100 bar (1000 kPa). Under such

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conditions the conversion of 3-hydroxypropanal is only about 90% while up to 10% is converted to byproducts.

It has also been proposed to combine the oxonation and hydrogenation steps into a one-step process with, it is claimed, minimal production of 3-hydroxypropanal as byproduct. Such a one-step process can be effected using a phosphine complex of cobalt carbonyl as the major catalyst ingredient. However, the use of a ruthenium compound as catalyst has also been proposed. An organic solvent is used in the reaction enabling a water extraction to be used in order to separate propane-1,3-diol from the oxonation mixture. Ethylene oxide conversions of 55% with a selectivity towards propane-1,3-diol of 87% are reported.

United States Patents Nos. 5,310,948 and 5,359,081 teach formation of β -propiolactone or polymers thereof by reaction of carbon monoxide and ethylene oxide in the presence of a cobalt-containing catalyst system comprising a source of cobalt and a hydroxyl-substituted pyridine.

Propane-1,3-diol can alternatively be produced from glycerol using recombinant bacteria expressing recombinant diol dehydratase. Such a process is taught in United States Patent Specification No. 5,821,092.

It has also been proposed to subject acrolein to hydration so as to form 3-hydroxypropanal which is then hydrogenated. In this connection reference may be made to United States Patent Specification No. 5,364,987.

In United States Patent Specification No. 5,334,778 it is proposed to produce propan-1,3-diol having a residual carbonyl content below 500 ppm by catalytically hydrogenating 3-hydroxypropanal in aqueous solution in the presence of a hydrogenation catalyst at 30°C to 80°C to a 3-hydroxypropanal conversion of 50% to 95% and then continuing the hydrogenation at 120°C to 140°C to achieve a 3-hydroxypropanal

conversion of substantially 100%.

Both glycerol and acrolein are, however, generally more expensive and less available than ethylene oxide. Hence it is not currently an economic proposition to manufacture propane-1,3-diol by either of these last two mentioned processes.

It would be desirable to provide an improved process for the production of propane-1,3-diol. It would further be desirable to provide a process for producing propane-1,3-diol by hydrogenation of an appropriate carbonyl compound which exhibits increased selectivity towards propane-1,3-diol and reduced amounts of undesirable byproducts, such as propan-1-ol, which cannot readily be converted to propane-1,3-diol. It would further be desirable to provide a process for the production of propane-1,3-diol by hydrogenation of an intermediate compound which can be made from ethylene oxide and which contains at least one carbon-oxygen double bond, such as 3-hydroxypropanal, β -propiolactone, oligomers of β -propiolactone, or an ester of 3-hydroxypropionic acid, with minimal formation of undesirable byproducts.

It is accordingly an objective of the present invention to provide an improved process for the production of propane-1,3-diol. In addition the present invention seeks to provide a hydrogenation process for producing propane-1,3-diol that uses in a hydrogenation step an optimised catalyst system. Yet a further objective of the present invention is to provide a process for the production of propane-1,3-diol by hydrogenation of an intermediate compound which can be made from ethylene oxide, such intermediate compound containing at least one carbon-oxygen double bond, and preferably being selected from 3-hydroxypropanal; β -propiolactone, oligomers of β -propiolactone, esters of 3-hydroxypropionic acid, and mixtures of two or more thereof, with reduced amounts being

formed of undesirable byproducts, such as propan-1-ol, which cannot readily be converted to the desired propane-1,3-diol.

According to the present invention there is provided process for the production of propane-1,3-diol which
5 comprises forming a vaporous feed mixture comprising a hydrogen-containing gas and a substantially anhydrous feedstock selected from 3-hydroxypropanal, β -propiolactone, oligomers of β -propiolactone, esters of 3-hydroxypropanoic acid, and mixtures of two or more thereof, supplying the
10 vaporous feed mixture to a hydrogenation zone containing a heterogeneous hydrogenation catalyst and maintained under hydrogenation conditions effective for hydrogenating feedstock to propane-1,3-diol, and recovering from the hydrogenation zone a reaction product comprising propane-1,3-
15 diol.

The feedstock to the hydrogenation step is substantially anhydrous, that is to say it contains no more than about 5% (w/v), preferably no more than about 1% (w/v), and even more preferably less than about 0.1% (w/v) of water. It is
20 selected from 3-hydroxypropanal, β -propiolactone, oligomers of β -propiolactone, and esters of 3-hydroxypropanoic acid, and mixtures of two or more thereof. β -propiolactone can self-polymerise to form oligomers of β -propiolactone. The presence of more than a minor amount of such oligomers in the
25 feedstock to the hydrogenation zone is generally undesirable because of their relative lack of volatility. Hence it will normally be preferred to use a feedstock to the hydrogenation zone which contains less than about 10 molar % of oligomers of β -propiolactone. Accordingly it will usually be preferred
30 to minimise the proportion of oligomers of β -propiolactone in the feedstock to the hydrogenation zone.

Hydrogenation is effected using a vaporous feed mixture to the hydrogenation zone, this mixture containing in

addition to the feedstock also a hydrogen-containing gas. The hydrogen-containing gas is preferably substantially free from carbon oxides but may contain one or more inert gases, such as nitrogen, argon and helium, in amounts of up to 50% v/v, but which preferably do not exceed about 10% v/v and more preferably do not exceed about 5% v/v, e.g. about 1% v/v or less.

The hydrogenation conditions may be selected so that the reaction mixture exiting the hydrogenation zone is also in the vapour phase. However, it is alternatively possible, and indeed may be preferable, to utilise hydrogenation conditions such that the reaction mixture at the exit end of the hydrogenation zone is below its dew point so that at least some of the condensable components thereof are present in the liquid phase.

The hydrogenation zone conveniently contains a fixed bed of a granular hydrogenation catalyst. If desired, the hydrogenation zone can contain more than one catalyst bed and the hydrogenation catalyst of one bed can, if desired, differ from the hydrogenation catalyst of at least one other bed.

The hydrogenation catalyst is preferably selected from noble metal catalysts, such as palladium catalysts, and copper-containing catalysts. More preferably the hydrogenation catalyst is a copper-containing catalyst. The active catalytic species in the hydrogenation catalyst may be at least partially supported on a supporting material selected from chromia, zinc oxide, alumina, silica, silica-alumina, silicon carbide, zirconia, titania, carbon, or a mixture of two or more thereof, for example, a mixture of chromia and carbon.

As examples of suitable copper-containing catalysts which may be utilised in the process of the invention there may be mentioned reduced copper oxide/zinc oxide

hydrogenation catalysts, reduced manganese-promoted copper catalysts, reduced copper chromite catalysts, and reduced promoted copper chromite catalysts.

Preferably the hydrogenation catalyst is a reduced manganese-promoted copper catalyst. Such manganese-promoted copper catalysts preferably have a total surface area of at least about 15 m²/g, more preferably at least about 20 m²/g, and even more preferably at least about 25 m²/g, in the unreduced form.

A particularly preferred hydrogenation catalyst is a reduced manganese-promoted copper catalyst which is available as DRD92/89A catalyst from Kvaerner Process Technology Limited of The Technology Centre, Princeton Drive, Thornaby, Stockton-on-Tees, TS17 6PY, England. Alternatively there may be used a reduced manganese-promoted copper catalyst which is available as DRD92/89B catalyst from Kvaerner Process Technology Limited.

The hydrogenation step is conducted under vapour phase feed conditions so that the feed stream to the hydrogenation zone is above its dew point and is thus a vaporous feed stream. The reaction product mixture from the hydrogenation zone can also be recovered at a temperature above its dew point so that it too is in vaporous form or it can be recovered at a temperature below its dew point so that at least part of the condensable components thereof are in liquid form.

Although it is possible to conduct the hydrogenation process of the present invention in a tubular reactor under substantially isothermal conditions, it will normally be preferred to operate under substantially adiabatic hydrogenation conditions using a fixed catalyst bed or beds since adiabatic reactors are much cheaper to construct than tubular reactors. However, care should be taken in designing

the plant, in particular in selecting a suitable gas:feedstock ratio and in choosing a catalyst size, that the temperature rise across any catalyst bed is limited to a reasonable value, typically not more than about 20°C, so as to keep the temperature to which the reaction mixture is exposed within desired limits. In this way the formation of 1-propanol as a byproduct can be limited.

It will normally be preferred that, in the vaporous feed stream to the hydrogenation zone, the hydrogen-containing gas:feedstock molar ratio shall be in the range of from about 50:1 to about 1000:1.

Typically the feed temperature to the hydrogenation zone is from about 130°C to about 180°C, more preferably from about 135°C to about 150°C, while the feed pressure to the hydrogenation zone is from about 50 psia (about 344.74 kPa) to about 2000 psia (about 13789.52 kPa), for example, from about 350 psia (about 2413.17 kPa) to about 1000 psia (about 6894.76 kPa). The feedstock is also preferably supplied to the first hydrogenation zone at a rate corresponding to a liquid hourly space velocity of from about 0.05 to about 5.0 h⁻¹. Preferably unreacted hydrogen-containing gas is recycled for further use.

If desired, the feedstock to the hydrogenation zone can be diluted with a solvent, such as methanol, which is stable under the hydrogenation conditions utilised.

The invention is further illustrated in the following Examples.

Example 1

This Example was intended to provide a simulation of conditions similar to those that might exist in a commercial hydrogenation reactor for hydrogenation of methyl 3-hydroxypropionate utilising recycled hydrogen which would be saturated with methanol co-product.

A solution of crude methyl 3-hydroxypropionate (approximately 90% pure) was diluted with an approximately equal weight of methanol to form a feed solution. This feed solution was subjected to vapour phase hydrogenation in a once-through adiabatic fixed-bed reactor. The reactor was constructed from a 95 cm length of 20.96 mm internal diameter tube which was oil-jacketed to reduce heat losses. The reactor contained a charge of 100 ml of DRD92/89A catalyst which is obtainable from Kvaerner Process Technology Limited of The Technology Centre, Princeton Drive, Thornaby, Stockton-on-Tees, TS17 6PY, England. The catalyst was reduced by a procedure analogous to that described in United States Patent Specification No. 5,030,609.

The feed solution was supplied at a feed rate of 12 ml/h to a heater and vaporised by a stream of pure hydrogen at a rate of 1000 Nl/h (i.e. 1000 litres per hour measured at 760 mm Hg [101.33 kPa] and 0°C). The vaporous mixture was passed over the catalyst at a pressure of 400 psig (2757.90 kPa gauge) and a temperature of 138°C. The reaction product mixture exiting the reactor was cooled and the condensed liquid collected. The feed and product were analysed by gas chromatography using a 60 metre CP SIL 19 capillary column of 0.32 mm internal diameter with a 1.3 µm film thickness.

Conversion of the methyl 3-hydroxypropionate was determined as 73.3% with a selectivity to propane-1,3-diol of 83.4% and to 1-propanol of 5.8%. It is believed that the byproducts comprise mainly materials which, upon hydrogenation, can be converted to propane-1,3-diol and hence can be recycled.

Example 2

The general procedure of Example 1 was repeated except that the temperature was 148°C. Conversion of the methyl 3-hydroxypropionate was determined as 84.9% with a

selectivity to propane-1,3-diol of 84.8% and to 1-propanol of 7.2%. Operation at this slightly higher temperature provides an expected increase in conversion with a minor increase in selectivity to 1-propanol.

5 Example 3

 The general procedure of Example 1 was repeated except that the temperature was 174°C. Conversion of the methyl 3-hydroxypropionate was determined as 99.95% with a selectivity to propane-1,3-diol of 13.1% and to 1-propanol of 81.8%. This shows that operation at high temperature favours formation of the alcohol, 1-propanol, rather than propan-1,3-diol.

Example 4

 The same feed solution as used in Example 1 was subjected to vapour phase hydrogenation in an adiabatic fixed-bed reactor system which incorporated recycle of excess gas following condensation of the reactor product stream. Make-up pure hydrogen was supplied to the system to maintain constant system pressure. The reactor was constructed from a 200 cm length of 26.64 mm internal diameter tube which was insulated and provided with electric trace heating means to prevent net heat loss from the reactor. The reactor contained a charge of 250 ml of DRD92/89A catalyst. The catalyst was reduced by a procedure analogous to that described in United States Patent Specification No. 5,030,609.

 The feed solution was fed at a rate of 80 ml/h to a heater and vaporised by a stream of mixed recycle gas and pure hydrogen at a rate of 10900 Nl/h. The vaporous mixture was passed over the catalyst at a pressure of 885 psig (6101.86 kPa gauge) and an inlet temperature of 149°C. The outlet temperature was measured as 150°C. The reactor product mixture was cooled and the condensed liquid

collected. The feed and product were analysed by gas chromatography using a 60 metre CP SIL 19 capillary column of 0.32 mm internal diameter with a 1.3 μ m film thickness.

Conversion of the methyl 3-hydroxypropionate was determined as 77.8% with a selectivity to propane-1,3-diol of 78.9% and to 1-propanol of 14.8%.

Example 5

The general procedure of Example 4 was repeated except that the inlet pressure was 735 psig (5067.65 kPa), and the mixed recycle and pure hydrogen make-up flow rate was 8116 Nl/h. Conversion of the methyl 3-hydroxypropionate was determined as 61.1% with a selectivity to propane-1,3-diol of 79.0% and to 1-propanol of 14.4%. Operation at this lower pressure and lower gas rate provides an expected reduced conversion but with similar selectivities to propane-1,3-diol and to 1-propanol.

Example 6

A solution of crude methyl 3-hydroxypropionate (approximately 98% pure) was diluted with an approximately equal weight of methanol to form a feed solution. This feed solution was subjected to vapour phase hydrogenation in the apparatus used in Example 4.

The feed solution was fed at a rate of 80.8 ml/h to a heater and vaporised by a stream of mixed recycle gas and pure hydrogen at a rate of 8717 Nl/h. The vaporous mixture was passed over the catalyst at a pressure of 885 psig (6101.86 kPa gauge) and an inlet temperature of 148°C. The outlet temperature was measured as 149°C.

The reactor product mixture was cooled and the condensed liquid collected.

The feed and product were analysed by the method used in Example 4.

Conversion of the methyl 3-hydroxypropionate was

determined as 71.3% with a selectivity to propane-1,3-diol of 80.6% and to 1-propanol of 12.5%. It is believed that the byproducts comprise mainly materials which, upon hydrogenation, can be converted to propane-1,3-diol and hence can be recycled.

Example 7

The general procedure of Example 6 was repeated except that the feed rate was 61.4 ml/h, the recycle stream was 6537 Nl/h and the inlet temperature was 149°C. The outlet temperature was measured as 150°C.

Conversion of the methyl 3-hydroxypropionate was determined as 84.1% with a selectivity to propane-1,3-diol of 73.7% and to 1-propanol of 21.5%.

Example 8

The general procedure of Example 7 was repeated except that the inlet temperature was 154°C. The outlet temperature was measured as 155°C.

Conversion of the methyl 3-hydroxypropionate was determined as 87.3% with a selectivity to propane-1,3-diol of 75.2% and to 1-propanol of 18.7%.

Example 9

The general procedure of Example 8 was repeated except that the mixed recycle and pure hydrogen make-up flow rate was 5226 Nl/h and the inlet temperature was 152°C. The outlet temperature was measured as 153°C.

Conversion of the methyl 3-hydroxypropionate was determined as 86.7% with a selectivity to propane-1,3-diol of 76.2% and to 1-propanol of 16.9%.

CLAIMS:

1. A process for the production of propane-1,3-diol which comprises forming a vaporous feed mixture comprising a hydrogen-containing gas and a substantially anhydrous feedstock selected from 3-hydroxypropanal, β -propiolactone, oligomers of β -propiolactone, esters of 3-hydroxypropanoic acid, and mixtures of two or more thereof, supplying the vaporous feed mixture to a hydrogenation zone containing a heterogeneous hydrogenation catalyst and maintained under hydrogenation conditions effective for hydrogenating feedstock to propane-1,3-diol, and recovering from the hydrogenation zone a reaction product comprising propane-1,3-diol.
2. A process according to claim 1, wherein the feedstock comprises an alkyl ester or a hydroxyalkyl ester of 3-hydroxypropanoic acid.
3. A process according to claim 1 or claim 2, wherein hydrogenation is effected using a fixed bed of a granular hydrogenation catalyst.
4. A process according to any one of claims 1 to 3, wherein the hydrogenation catalyst is selected from noble metal catalysts and copper-containing catalysts.
5. A process according to claim 4, wherein the hydrogenation catalyst is a copper-containing catalyst.
6. A process according to claim 5, wherein the copper-containing catalyst is selected from reduced copper oxide/zinc oxide hydrogenation catalysts, reduced manganese-promoted copper catalysts, reduced copper chromite catalysts, and reduced promoted copper chromite catalysts.
7. A process according to claim 5 or claim 6, wherein the copper-containing catalyst is a reduced manganese-promoted copper catalyst.
8. A process according to any one of claims 1 to 7, wherein

the hydrogen-containing gas:feedstock molar ratio in the vaporous feed mixture is in the range of from about 50:1 to about 1000:1.

9. A process according to any one of claims 1 to 8, wherein
5 the feed temperature to the hydrogenation zone is from about 130°C to about 180°C.

10. A process according to claim 9, wherein the feed temperature to the hydrogenation zone is from about 135°C to about 150°C.

10 11. A process according to any one of claims 1 to 10, wherein the feed pressure to the hydrogenation zone is from about 50 psia (about 344.74 kPa) to about 2000 psia (about 13789.52 kPa).

12. A process according to claim 11, wherein the feed
15 pressure to the hydrogenation zone is from about 350 psia (about 2413.17 kPa) to about 1000 psia (about 6894.76 kPa).

13. A process according to any one of claims 1 to 12, wherein the feedstock is supplied to the first hydrogenation zone at a rate corresponding to a liquid hourly space
20 velocity of from about 0.05 to about 5.0 h⁻¹.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 01/01128

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C29/141 C07C29/149 C07C29/16 C07C31/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 094 914 A (ROTTIG WALTER ET AL) 13 June 1978 (1978-06-13) column 1, line 25 - line 64 column 2, line 35 - line 61; claims; example 3	1-13
X	EP 0 857 709 A (DEGUSSA) 12 August 1998 (1998-08-12) page 3, line 26 - line 27 page 5, line 22 - line 23	1-13
X	DE 37 37 277 A (UNION CARBIDE CORP) 19 May 1988 (1988-05-19) page 2, line 24 - line 30 page 5, line 49 - line 53 page 5, line 65 -page 6, line 22	1-13
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 01/01128

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 511 744 A (MIYAZAKI HARUHIKO ET AL) 16 April 1985 (1985-04-16) column 1, line 7 - line 10 column 1, line 37 - line 42 column 4, line 53 - column 5, line 35; claims -----	1-13
A	US 4 855 515 A (MORRIS DON L ET AL) 8 August 1989 (1989-08-08) column 3, line 40 - column 4, line 46 -----	1-13
A	US 5 030 609 A (TURNER KEITH ET AL) 9 July 1991 (1991-07-09) cited in the application abstract; example 11 -----	1-13
A	US 3 770 837 A (FAVSTRITSKY N ET AL) 6 November 1973 (1973-11-06) claims; examples -----	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 01/01128

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4094914 A	13-06-1978	DE 2054601 A	10-05-1972
		AT 313247 B	15-01-1974
		AU 3517071 A	03-05-1973
		CA 948217 A	28-05-1974
		FI 55646 B	31-05-1979
		FR 2113422 A	23-06-1972
		GB 1363677 A	14-08-1974
		IT 942249 B	20-03-1973
		JP 51018928 B	14-06-1976
		RO 63376 A	15-07-1978
		SE 391919 B	07-03-1977
EP 0857709 A	12-08-1998	DE 19703383 A	06-08-1998
		JP 10212253 A	11-08-1998
		US 6140543 A	31-10-2000
DE 3737277 A	19-05-1988	US 4762817 A	09-08-1988
		AT 68460 T	15-11-1991
		AU 610529 B	23-05-1991
		AU 8059187 A	05-05-1988
		BE 1000439 A	06-12-1988
		BR 8705856 A	14-06-1988
		CA 1311739 A	22-12-1992
		CN 87108109 A,B	15-06-1988
		CN 1050994 A,B	01-05-1991
		CS 8707873 A	13-05-1992
		DE 3773854 A	21-11-1991
		DK 572787 A	04-05-1988
		EP 0269888 A	08-06-1988
		ES 2005050 A	16-02-1989
		FI 874830 A,B,	04-05-1988
		FR 2606013 A	06-05-1988
		GB 2199766 A,B	20-07-1988
		HU 45472 A,B	28-07-1988
		IN 170293 A	07-03-1992
		IT 1223344 B	19-09-1990
		JP 1085936 A	30-03-1989
		JP 5057251 B	23-08-1993
		JP 2655034 B	17-09-1997
		JP 5253482 A	05-10-1993
		KR 9201303 B	10-02-1992
		KR 9203916 B	18-05-1992
		NL 8702620 A	01-06-1988
		NO 874583 A,B,	04-05-1988
		SE 8704297 A	04-05-1988
		SG 124292 G	19-02-1993
		SU 1731040 A	30-04-1992
		US 4876402 A	24-10-1989
		YU 199587 A	30-04-1989
		YU 210988 A	30-04-1990
		ZA 8708258 A	02-05-1988
US 4511744 A	16-04-1985	JP 1446856 C	30-06-1988
		JP 58193735 A	11-11-1983
		JP 62056785 B	27-11-1987
		CA 1206135 A	17-06-1986
		DE 3316485 A	10-11-1983
		FR 2526419 A	10-11-1983

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 01/01128

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4511744 A		GB 2121310 A,B	21-12-1983
US 4855515 A	08-08-1989	NONE	
US 5030609 A	09-07-1991	CA 1325419 A	21-12-1993
		CN 1031336 A,B	01-03-1989
		DE 3868299 A	19-03-1992
		EP 0301853 A	01-02-1989
		ES 2030866 T	16-11-1992
		IN 172702 A	13-11-1993
		JP 1127042 A	19-05-1989
		JP 2704413 B	26-01-1998
		KR 9612095 B	12-09-1996
		MX 170426 B	23-08-1993
		RU 2028194 C	09-02-1995
US 3770837 A	06-11-1973	NONE	